212. Photodecomposition of Liquid Water with TiO_2-Supported Noble Metal Clusters

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Summary

Rh- and Ru-loaded TiO_2-particles were produced from cluster precursors ($Rh_6(CO)_{16}$, $Ru_3(CO)_{12}$) and their activity in mediating H_2O-decomposition through band-gap excitation was investigated. Activity increases in the order $Ru < RuO_2 < Rh \simeq Rh_2O_3$. Bifunctional Rh/$RuO_2$-loaded TiO_2 exhibits optimal performance with overall light-to-chemical-energy conversion efficiency of 0.13%. Lack of O_2-appearance in the gas phase during photolysis observed with closed systems is due to photo-uptake of O_2 by the TiO_2-particles. In alkaline solution the capacity for O_2-uptake is surprisingly high and the nature of the stored O_2 is tentatively identified as a μ-peroxo-bridged Ti-species.

Introduction. – Supported metal catalysts have previously been shown to be active in microheterogeneous systems that achieve H_2O-cleavage by visible and UV light [1–10]. Noble metals deposited onto semiconductors such as TiO_2 [1–3] [7], $SrTiO_3$ [4–6] and CdS [8] [9] appear to be particularly promising. To achieve optimum activity in H_2O-decomposition, high dispersion of the noble metal onto the support is generally required. This increases the H_2O-reduction and -oxidation rates per unit mass of catalyst employed. Moreover, there is recent evidence [11] that the recombination of H_2 with O_2 might be affected by the size of the noble-metal particle. Thus, it has been shown that the reduction of O_2 on Pt-cathodes tested for fuel cell application is almost totally inhibited once the Pt-crystallite size decreases below 30 Å. Reduction of O_2 to H_2O is an undesirable back reaction in devices that afford simultaneous generation of H_2 and O_2 by light. In close relation to this effect stands the observation of *Turkevich et al.* [12] that the activity of Pt-colloids in the catalytic decomposition of H_2O_2 drops from an extremely high value (close to that of catalase) to practically zero when the particle size was decreased below 30 Å.

A particularly favorable situation for H_2O-decomposition would arise if these ultrafine Pt-particles, though inactive in O_2-reduction, would still remain powerful catalysts for the generation of H_2 from H_2O. That this concept is viable was shown by us in a recent investigation [13] where a systematic test of the effect of Pt-particle size on the rate of photochemical H_2-generation in Pt/TiO_2-dispersions was carried out. The activity of 8-Å-sized Pt-particles was found to be much superior to that of 30-Å aggregates. In the present investigation, the catalytic behavior of cluster-sized Rh- and Ru-aggregates supported onto TiO_2 is scrutinized. A recently established method [14] [15] involving thermal decomposition of noble-metal carbonyl compounds is for the first time applied to produce highly active catalysts for H_2O-cleavage. These investigations confirm also the O_2-carrier function assumed by the TiO_2-particles in these systems.

Experimental. – The TiO_2 used in these experiments was supplied by *Degussa* (*P-25*, surface area 50 ± 15 m^2 g^{-1}). Earlier studies showed that this material is of high quality and purity and, hence, it was used as such. The $Rh_6(CO)_{16}$ and $Ru_3(CO)_{12}$ are from *Ventron GmbH* and *Fluka AG*, respectively, and were used without any further purification. Hexane *(Fluka, p.a.)* and $CHCl_3$ *(Fluka, p.a.)* were of spectroscopic purity.

1. *Preparation of Rh/TiO$_2$*. Required amount of $Rh_6(CO)_{16}$ is dissolved in $CHCl_3$ and mixed with TiO_2 to form a slurry. Care is taken to see that excess solvent is not used to avoid localized high concentration of the carbonyl. After impregnation the sample is outgassed at 40° to remove the solvent and subsequently dried at 100° for 1 h. The material is then activated in flowing Ar at 450° for 2 h, followed by cooling to r.t. in Ar. This procedure is expected to yield highly dispersed zero-valent Rh on the support. However, due to the presence of hydroxyl groups on the surface, a small portion of the metal may be oxidized by the metal support interaction [16].

2. *Preparation of Ru/TiO$_2$*. Supported Ru-catalysts are prepared by impregnating the support with $Ru_3(CO)_{12}$ from hexane solution followed by outgassing, drying and activation at 400°.

RuO$_2$/TiO$_2$. Ru/TiO_2 prepared as described above is heated in O_2-flow at 400° for 1 h.

RuO$_2$/Rh/TiO$_2$. RuO_2/TiO_2-catalyst prepared earlier is impregnated with $Rh_6(CO)_{16}$ as described earlier and activated.

Due to the low solubility of these carbonyls in the solvents, higher-loading catalysts have to be prepared in stages to adhere to the incipient wetness technique, *i.e.* part of the carbonyl is dissolved in sufficient solvent to form the slurry with the support and impregnated as above. The sample, after drying at 100°, is again impregnated with more of the carbonyl and so on. Once the impregnation is complete, the catalyst activation in Ar is performed.

3. *Photolysis Experiments*. The photoactivity of the catalysts is tested by irradiating 50 mg of the sample with 25 ml of the solution in a *Pyrex* flask with an optically flat light-entry window of 3-cm^2 surface. The cell has three outlets all of which can be closed by glass stopcocks, thereby eliminating any organic matter coming in contact with the solutions. Irradiations were carried out in the sample compartment of a *Hanau 1000 W* suntest system using a 320-nm cutoff filter to remove UV light. The total irradiance over UV, visible and IR was approx. 90 mW/cm^2. This flux and its spectral distribution match closely *AM 1* solar radiation. During illumination, the temperature of the solution rose to 30–35°. Prior to irradiation, the solutions were deaerated with Ar for 10 min. The products are analyzed by GC using thermal conductivity detectors and a carbosieve 5-Å column.

O$_2$-Uptake Experiments. The reaction system is degassed in Ar as described earlier and 1 ml O_2 is injected into it. The solution is now irradiated, and the O_2 present in the system is estimated at frequent intervals. After 18 h, when a substantial amount of H_2 is formed, the system is degassed in Ar, another 1 ml O_2 injected and the tests continued as above. The cycle is repeated until the O_2-uptake and H_2-generation have practically ceased.

Results. – TiO_2/P-25 alone, when dispersed in H_2O, shows no photoactivity under illumination by simulated sunlight. On the other hand, when loaded with Rh- and/or Ru-clusters, rather active catalysts are obtained as indicated by the rapid generation of H_2 under illumination. *Figure 1* shows the amount of H_2 obtained as a function of irradiation time for different types of catalyst. The loading of TiO_2 with noble metal was 0.3% and the pH kept at 14. Activity increases in the order $Ru < RuO_2 < Ru/Rh < Rh < Rh/RuO_2$. Best results were obtained with a

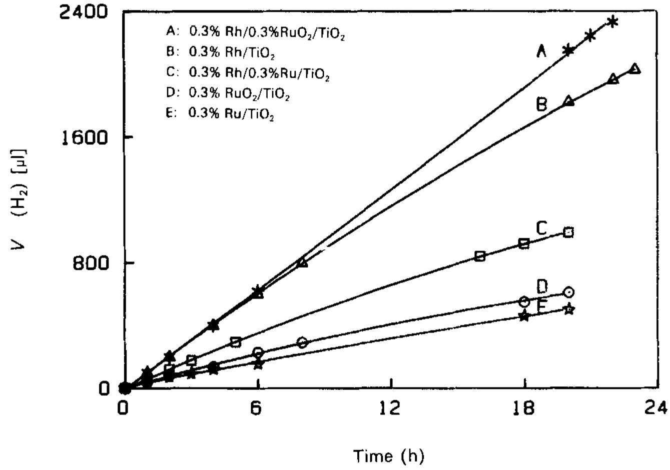

Fig. 1. *H_2-generation by photolysis of H_2O on TiO_2-supported Rh- and Ru-catalysts.* Reaction temperature 30°, pH 14. Volume of H_2 (1 atm. T = 298 K) is plotted as a function of irradiation time.

bifunctional catalyst containing Rh and RuO_2 at 0.3% each, where H_2 is generated initially with a rate of 0.1 ml/h. Based on the *total* incident light flux and the standard enthalpy of combustion of H_2, this value corresponds to an overall power conversion efficiency of *ca.* 0.13%. Note that the activity of the catalyst is sensitive to the oxidation state of the cluster. Thus, Ru/Rh is inferior to RuO_2/Rh. The latter is also superior to a combination of Rh_2O_3/RuO_2 (not shown). Apart from the efficiency of H_2-generation, these catalysts can also be distinguished by the maximum amount of H_2 that can be produced in a closed vessel before photogeneration ceases ($V_{max}[H_2]$). This maximum volume is reached within 18–24 h for all the catalysts employed and is related to the initial rate of H_2-generation ($r(H_2)$): The higher $r(H_2)$, the more H_2 can be built up under irradiation. The largest amount of H_2 (*ca.* 2.5 ml) is obtained with the $TiO_2/Rh/RuO_2$ bifunctional redox catalyst.

If the illumination is interrupted once the volume of H_2 approaches its plateau value and photogeneration of H_2 ceases to occur; the initial H_2O-cleavage activity of the catalyst can be restored by bubbling the dispersion with N_2 or Ar. Thus, in a typical experiment employing Rh/TiO_2, $r(H_2)$ was initially 75–90 µl/h and dropped after 22 h when 2 ml H_2 had been generated. Irradiation was interrupted at this time and the solution flushed with N_2 for 15 min. Subsequent illumination generated H_2 at practically the same initial rate as in the first run and $V(H_2) = 1.8$ ml was again reached after 20 h. In a parallel experiment, the first irradiation period was extended to 24 h, *i.e.* several hours longer than required to reach the plateau value for the H_2-volume. However, in this case N_2-flushing did not restore the initial H_2O-cleavage activity. H_2-generation in the second cycle resumed here only with a rate of 40 µl/h and dropped to zero within a few hours of irradiation. The inactive catalyst was centrifuged at this point and subjected to Ar-treatment at 300°. This procedure restored *ca.* 40% of its original activity.

Figure 2 shows the effect of Rh-loading of TiO_2 on the activity of the catalyst. Both $r(H_2)$ and $V_{max}(H_2)$ increase with Rh-content until at 0.3% a maximum is reached from where on a sharp decline is noted. At 0.6% loading the H_2-generation rate as well as $V_{max}(H_2)$ have already decreased severalfold with respect to optimum activity of the catalyst.

The effect of pH on the H_2O-cleavage activity of the Rh-loaded TiO_2 was also investigated and is illustrated in *Figure 3*. The performance of the catalyst in acidic

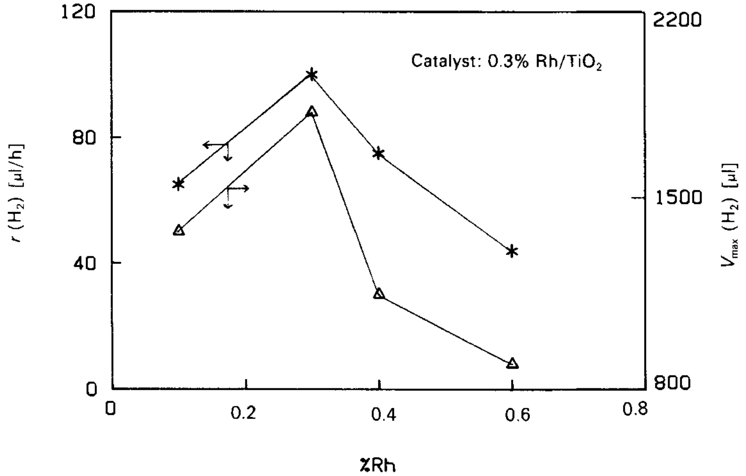

Fig. 2. *Effect of Rh-loading on* $r(H_2)$ *(*) and* $V_{max}(H_2)$ *(△) obtained with* Rh/TiO_2*-catalysts.* %-Rh by weight with respect to TiO_2, reaction temperature 30°, pH 14.

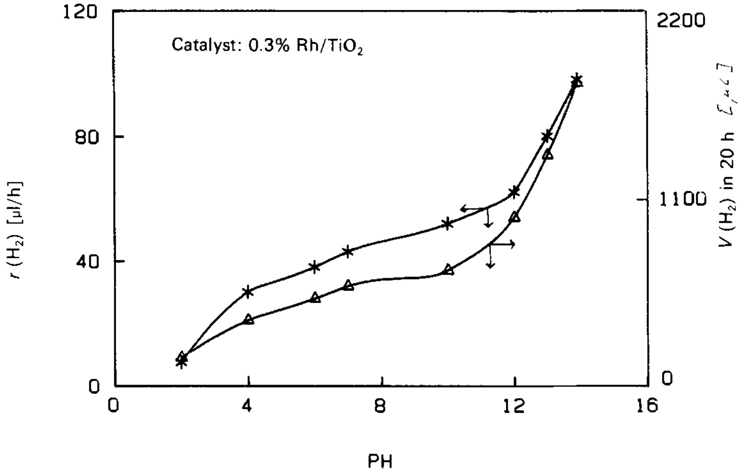

Fig. 3. *Effect of pH on* $r(H_2)$ *(*) and* $V_{max}(H_2)$ *(Δ) obtained with 0.3%* Rh/TiO_2*-catalyst.* Reaction temperature 30°.

solution is very poor. $r(H_2)$ is small and very little H_2 can be built up. Both $r(H_2)$ and $V_{max}(H_2)$ increase sharply between pH 2 and 4, which is followed by a plateau region extending until pH 12. There is a second strong increase in both parameters between pH 12 and 14. Use of higher basicity (2–5 M NaOH) did not lead to any further changes in $r(H_2)$ and $V_{max}(H_2)$.

GC analysis showed that no or very little O_2 appeared in the gas phase during all these photolysis experiments which were performed in a closed system under 1 atm pressure. To further investigate this effect, we examined the photo-uptake of O_2 by Rh (0.3%)/TiO_2-dispersions (pH 14). After degassing the sample with Ar[1], 1 ml of O_2 was injected and the solution irradiated with the sunlamp. *Figure 4* shows that 6 h of irradiation sufficed to remove 75% of the injected O_2. At this point photogeneration of H_2 commenced and continued until $V_{max}(H_2) = 1.4$ ml was reached after *ca.* 21 h of total illumination time. In *Figure 4* the irradiation was interrupted already after 18 h and after flushing for *ca.* 15 min with Ar the injection of O_2 was repeated. Renewed exposure to light led to O_2-uptake and H_2-formation kinetics identical to those observed in the first run. This cycle was repeated 4 times without noticeable changes. In the fifth run, we deliberately extended the illumination period to 24 h, *i.e.* 4 h longer than required to attain $V_{max}(H_2)$. Irradiation in

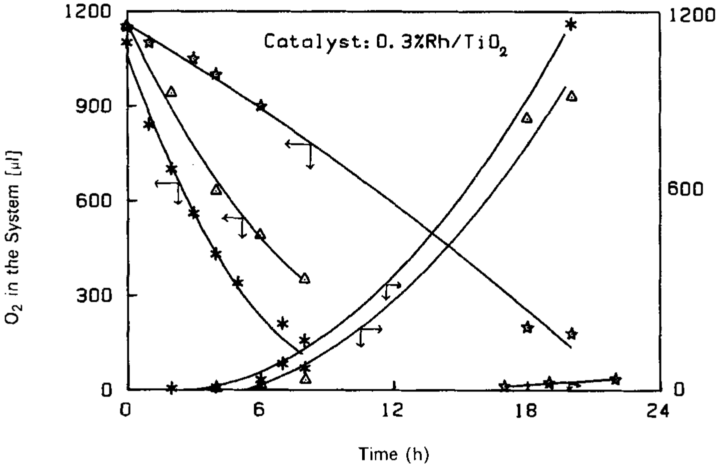

Fig. 4. *Decrease of O_2- and increase of H_2-volume during the photolysis of aq. Rh (0.3%)/TiO_2 suspensions.* Temperature: 30°, pH 14; H_2-evolution starts at low concentration of O_2, the rate of which increases significantly once all the O_2 is consumed.

*: the rate of O_2-disappearance and H_2-evolution in the first four cycles consisting of 4 consecutive O_2-injections of 1 ml each, every time degassing the system in Ar for 15 min, once *ca.* 1.2 ml H_2 is produced. For the fifth cycle, H_2-generation was allowed to continue for 24 h and reach the plateau.

△: O_2-photo-uptake and H_2-generation for the sixth cycle after the introduction of 1 ml O_2 and interrupting the illumination after $V_{max}(H_2) \approx 1$ ml was reached.

☆: O_2-photo-uptake and H_2-formation for the seventh cycle.

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[1] Replacing Ar by N_2 gave practically the same results.

the plateau for $V(H_2)$ spoils the catalysts' activity for both O_2-photo-uptake and H_2-generation which can not be restored by Ar-bubbling. *Figure 4* shows that within 6 h of irradiation only 50% of the injected O_2 (*ca.* 1.1 ml) was consumed in the 6th cycle. H_2-photogeneration occurred also more slowly and ceased after 20 h when $V_{max}(H_2) = 1$ ml was attained. After renewed bubbling with Ar, O_2-photo-uptake was drastically retarded and only traces of H_2 were photogenerated.

Discussion. – Band-gap excitation of TiO_2-particles produces electron-hole pairs and the conduction-band position of anatase is sufficiently negative to allow for H_2-generation *via*

$$2e^-_{CB} + 2\,H^+ \rightarrow H_2 \tag{1}$$

while the complementary hole reaction is known to be [17]

$$4h^+ + 2\,H_2O \rightarrow 4\,H^+ + O_2 \tag{2}$$

Reaction 1 requires a high overvoltage on bare TiO_2 but can be accelerated by noble-metal catalysts. The role of Rh or Ru in our system is therefore to enhance the H_2-generation step. In the case of Rh/TiO_2, the H_2O-cleavage activity is insensitive to the degree of oxidation, which differs from results [5] obtained with $Rh/SrTiO_3$. In contrast, the activity of Ru-loaded TiO_2 is affected by the degree of oxidation of the noble metal, since RuO_2/TiO_2 gives much better H_2-yields than Ru/TiO_2. We attribute this effect to hole scavenging by RuO_2 and subsequent catalysis of H_2O-oxidation *via Reaction 2*. However, recent results by *Gissler & McEvoy* [18] and our findings [19] indicate that RuO_2-deposits on semiconductors may also enhance the reduction of H_2O by conduction band electrons. Nevertheless, from the fact that optimum results were obtained with bifunctional Rh/RuO_2-loaded TiO_2-particles, it is unlikely that the same event is catalyzed by both deposits.

The fate of O_2 in our H_2O-photolysis system should be discussed in more detail now. TiO_2 is known to photoadsorb O_2 from the gas [20] as well as liquid phase [21] *via* the conduction-band process

$$O_2 + e^-_{CB} \rightarrow O_2^- \tag{3}$$

which generates superoxide radicals as a primary product. In aq. TiO_2-dispersions *Reaction 3* occurs *via* surface states [22] constituted by basic hydroxyl groups[2]) at the particle surface. (In acidic aq. solutions, these surface states can be moved into the conduction band, and therefore eliminated to a large part, *via* addition of Na_2SO_4 [23].)

Alkaline solutions of O_2^- are quite stable [24], but in the presence of TiO_2 specific adsorption to the particle surface is expected to occur. (During chemisorption, a fraction of the negative charge carried by O_2^- may be transferred to the Ti^{4+}-site with which it interacts.) The lack of appearance of O_2 in the gas phase

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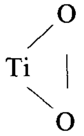
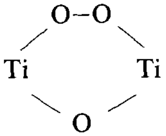
[2]) According to *Böhm* [25] there exists two types of OH on the surface of anatase. The pH for the acidic type is 2.9, that for the basic type is 12.7.

can therefore be rationalized in terms of efficient photo-uptake of O_2 by the TiO_2-particles. The rate of O_2-adsorption and maximum capacity for O_2-storage by the TiO_2-particles have a decisive influence on the overall efficiency of H_2O-photodecomposition. Thus, the steep increase of $r(H_2)$ and $V_{max}(H_2)$ around pH 3 and 13 is evidently related to the ionization of surface hydroxyls (pK 2.9 and 12.7 [25]) which play a crucial role in the photo-uptake of O_2 [22] [23]. Assuming that the number of binding sites available at the TiO_2-surface equals that of basic hydroxyl groups, the maximum capacity of *P-25* powder for O_2-chemisorption is predicted [25] to be *ca.* 230 µmoles or 5.4 ml/g. Our experiments employed 50 mg TiO_2/*P-25* which should be able to bind *ca.* 0.27 ml of O_2 as O_2^-. Therefore, $V_{max}(H_2)$ should be at most 0.54 ml. As shown in *Figure 3*, $V_{max}(H_2)$ stays within this limit only in neutral or acidic solution while in alkaline medium up to 5 times higher amounts of H_2 are obtained. Similarly, the observed photoconsumption of 1–1.2 ml O_2 at pH 14 and formation of additional 1.6 ml H_2 indicates that the maximum capacity for O_2-uptake is close to 2 instead of 0.27 ml. Assuming monolayer coverage of the particles, the distance of adjacent O_2^--groups at 2 ml/50 mg TiO_2-loading would be 2.3 Å. Such a high surface concentration of O_2 is expected to favor formation of peroxo compounds. Ti-ions are particularly prone to form such peroxo complexes. Structures with one peroxo group per Ti-ion, *i.e.*



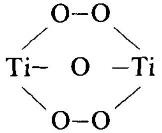
I

or its dimer [26] have to be distinguished from μ-peroxo species such as [27]



II

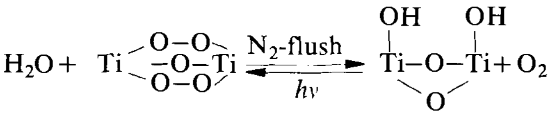
which is produced from H_2O_2 and TiO_2 in hot alkaline solution and has a yellow color. Chelates with two μ-peroxo bridges, *i.e.* **III**



III

has also been suggested and such a structure should be free of strain [26].

Preliminary experiments showed that **II** and/or **III** are likely to be products of O_2-photo-uptake in alkaline solution. Irradiated solutions display a faint yellow color after centrifugation indicating the presence of μ-peroxo Ti-dimers. Such compounds should be amenable to reoxidation by permanganate in acidic medium [27]. Indeed, both the supernatant as well as the catalyst powder reduced $KMnO_4$ dissolved in 1 N H_2SO_4. In contrast, a blank experiment with a catalyst dispersion that had not been irradiated showed no permanganate consumption. At least 30% of the total amount of O_2 produced during H_2O-photolysis could be accounted for by the formation of peroxo complexes present at the surface of the TiO_2-particles and in solution. This value represents only a lower limit since part of the peroxides may decompose during the analytical treatment of the samples. Thus, we found that bubbling of the supernatant with N_2 reduces significantly the amount of peroxo complexes detectable by $KMnO_4$-oxidation. This indicates that decomposition of the peroxides takes place during the flushing with N_2 which may be accounted for by processes such as



$$H_2O + \mathrm{Ti}\begin{matrix} \diagup O-O \diagdown \\ -O-O- \\ \diagdown O-O \diagup \end{matrix}\mathrm{Ti} \underset{h\nu}{\overset{N_2\text{-flush}}{\rightleftarrows}} \underset{\diagdown O \diagup}{\overset{OH}{\overset{|}{\mathrm{Ti}}}-O-\overset{OH}{\overset{|}{\mathrm{Ti}}}} + O_2 \qquad (4)$$

These reactions are presently investigated in more detail.

Conclusions. – The present paper introduced the technique of metal cluster decomposition as a new strategy to prepare highly dispersed TiO_2-based catalysts suited for light-induced H_2O-decomposition. Light-energy conversion efficiencies achieved approach the limits expected for UV-light-absorber-based systems. The O_2-carrier function of the TiO_2-particles deduced earlier from visible light induced H_2O-decomposition studies is confirmed. Clues are also obtained as to the nature of the reduced oxygen species which is tentatively identified with μ-peroxo-bridged Ti-complexes. The use of O_2-carriers of this type may well be a viable concept to overcome the H_2/O_2 separation problem inherent to these systems.

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